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COATINGS. ENAMELS

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DECORATIVE ENAMELS ON PRECIOUS METALS

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It is shown that the market is interested in high-quality enamel frits suitable for artistic painting on metal. Brief historical information on enameling is given. The compositions of enamels must be studied more thoroughly in order to re-establish the technique of artistic enameling. The requirements for such materials are formulated. A method for synthesizing the materials in the laboratory is described and their properties are indicated.

Key words: enamel, enameling, compositions, frit, enameling technology.

Interest in restoring the technique of artistic enameling, which has been known since ancient times and has risen and fallen during different periods in history and in different countries, has appeared in recent years in the jewelry industry. There are several versions of the origin and development of hot-enamel technology.

According to the most popular version, this technology originated in the Middle East, approximately in the 10 – 11th centuries A. D. In the other version, the technology for fabricating articles by the “cloisonné enamels” technique belongs to the 4th century — when the Byzantine Empire started to flower.

But the real flowering of the technology occurred much later in China at the end of the 12th and middle of the 13th centuries. The first finds of articles made by the hot-enameling technology were made during the Yuan dynasty (1271 – 1368). The emperor of the next dynasty — Ming (1368 – 1644) showed interest in bronze castings decorated with hot enamels. This is the period when a special light-blue enamel composition known as Jingtai Blue came to embody Chinese application art as Gzhel’ embodies Russian ceramics art [1 – 3].

In Russia, cloisonné enamel articles appeared in Russia during the Kievan Rus’ period [4]. The technology developed and improved over many centuries and reached its pinnacle at the end of the 19th and beginning of the 20th centuries in the workshops of Carl Peter Fabergé. The court jeweler clearly understood the possibilities which enameling opened up and he used them extensively. He devised articles requiring enameling quite large surfaces (en plein technique) and rounded surfaces (en ronde bosse technique). Up to 144 main enamel colors were used in the articles made in Fabergé‘s workshops. Fabergé became world famous because of a series of Imperial Easter eggs. Nine of them are stored in the Armory in the Kremlin in Moscow.

When the First World War started in 1914, because of mobilization Fabergé‘s workshops started to feel a shortage of qualified craftsmen. The company’s Moscow division, which worked with silver, switched to making hand grenades and cartridge casings for artillery shells. The firm closed for a time, resuming work in 1918. The revolutionary events and accompanying disorder in Russia destroyed the great jeweler’s workshops together with all records and prescriptions. The master himself left Russia and settled in Europe, where he soon died [5].

During the Soviet period attempts to restore the technique of hot enameling were made next to glassmaking plants, the best results being achieved by the craftsmen at the “Druzhnaya gorka” plant. They obtained 14 chemically stable decorative enamels, but in the 1990s work on enamels ceased, and once again the prescriptions were lost. Today, the only large producer of colored enamels in Russia is the Dulev plant. Aside from its products, English, French, and Austrian enamels are present in the Russian market (the Lasso firm supplies them to the Russian market).

However, the frits produced at the present time do not meet the stringent requirements of the jewelry industry and are unsuitable for painting on metals. Their main drawback is that the enamels separate from the substrate and color is lost

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as a result of repeated firing as well as inadequate resistance to acid solutions. On this basis and taking account of all technological stages in the creation of articles of jewelry, requirements have been formulated for the composition of enamels for precious metals.

– The linear thermal expansion coefficient (CLTE) of the enamel must fall within the range $(100 - 120) \times 10^{-7}\ K^{-1}$. This is necessary to obtain a strong metal – enamel bond.

– The enamel must be chemically stable with respect to a weak solution of hydrochloric acid. This is due to the particulars of the technology used to deposit enamel, where after firing the article is placed in acid in order to remove the oxide film formed on the part of the metal which remained uncovered by glaze (whitening of the metal).

– The enamel must have good flowability along the surface of the metal at quite low temperatures — not exceeding 790°C. This is because above 800°C the soldered junctions of an article of jewelry begin to melt and the article itself deforms.

A review of sources in the literature devoted to the problems of creating enamels on precious metals revealed many compositions which are described in patents, inventor's certificates, journal articles, and so forth. According to the published data, practically all enamels are 80%[3] silicon and lead oxides, whose fraction in the material is approximately the same. Aside from the components indicated, glass contains approximately 10% potassium oxide, as a modifying agent, as well as small quantities of the oxides of boron, zinc, sodium, barium, tin, and many others. The fraction of each component could reach 5%. To evaluate their suitability as enamels on precious metals, glasses with more than 40 different compositions were made.

The batch for obtaining enamels consisted of "pure" and "analytically pure" grade raw-material components. Powders were carefully mixed in a porcelain mortar to obtain a uniform mixture. To decrease losses of volatile components during melting, the crucibles together with the charge were placed inside a hot laboratory furnace, heated to 1400°C, and held in the furnace for 30 min. This time was sufficient to heat the batch, melt and dissolve the components, and form a uniform clear melt. The furnace itself is a laboratory apparatus with an approximately 150 × 150 × 300 mm work-space, heated by silicon carbide heaters. A platinum thermocouple was used to determine the temperature in the furnace.

[3] Here and below the content by weight.

Multicomponent glasses were studied. Their compositions fluctuated in the following ranges: 36.9 – 43.8% SiO_2, 36.3 – 41.8% PbO, 7.8 – 16.5% K_2O, 0 – 1.0% Al_2O_3, 0 – 1.0% B_2O_3, 0 – 0.3% Na_2O, 0 – 3.5% BaO, 0 – 1.0% CaO, 0 – 1.0% SnO, 0 – 6.2% ZnO, and 0 – 1.0% Sb_2O_3. The glass was formed into 30 – 50 mm in diameter disks (they were used to determine the physical–chemical properties) and frits (for deposition on a metal substrate). In many experiments, copper plates were used as substrates for deposition of enamel. It is believed that successful flow and setting of a composition on copper guarantees that this composition can be used for enameling silver and gold. Most of the enamels studied were found to be unsuitable for deposition on precious metals in the jewelry business either because the deposition temperature (above 800°C) is too high or the acid resistance of the enamels is too low.

The difficulty of solving the problem lay in the fact that the components of the glass which lower the deposition temperature of the enamel and increase the enamel's CLTE, approaching that of the metal substrate, also lower the acid resistance of the enamel.

The problem was solved by adjusting the ratios between all components of the material. The experimental work led to the development of a composition of an artistic enamel for precious metals (silver and copper), which possesses good flowability on these metals at temperatures near 790°C, preserving the strong bond with the metal surface as an article cools and possessing adequate chemical resistance in order to withstand without visible damage the whitening of the metal in dilute hydrochloric acid. Silicon and lead oxides comprise the largest fraction in the composition developed (> 80%), potassium oxide is the modifying agent, and small quantities of boron, tin, antimony, zinc, and barium oxides also enter into the enamel.

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